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# Ortho-H<sub>2</sub> and the age of interstellar dark clouds

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## ABSTRACT

Interstellar dark clouds are the sites of star formation. Their main component, dihydrogen exists under two states, ortho and para. H<sub>2</sub> is supposed to form in the ortho:para ratio (OPR) of 3:1 and to subsequently decay to almost pure para-H<sub>2</sub> (OPR  $\leq$  0.001). Only if the H<sub>2</sub> OPR is low enough, will deuteration enrichment, as observed in the cores of these clouds, be efficient. The second condition for strong deuteration enrichment is the local disappearance of CO, which freezes out onto grains in the core formation process. We show that this latter condition does not apply to DCO<sup>+</sup>, which, therefore, should be present all over the cloud. We find that an OPR  $\geq$  0.1 is necessary to prevent DCO<sup>+</sup> large-scale apparition. We conclude that the inevitable decay of ortho-H<sub>2</sub> sets an upper limit of  $\sim$ 6 million years to the age of starless molecular clouds under usual conditions.

*Subject headings:* ISM: abundances — ISM: clouds — evolution — ISM: molecules — astrochemistry

## 1. Introduction

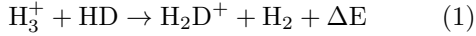
The low mass star formation process is relatively well understood, however its first step details remain uncertain, especially regarding the question of time and age. Still much debated questions are: how long it takes for a cloud to form from the diffuse atomic medium, how long a molecular cloud lives, how long it takes to form a condensation that will evolve into a prestellar core that subsequently collapses to form a proto-star. Today, much debate exists upon the lifetime of clouds, e.g. Hartmann et al. (2001) defending a short lifetime (1 to a few million years) while Tassis & Mouschovias (2004) and Mouschovias et al. (2006) claim a typical age of 10 million years, but

most arguments are either of limited statistical significance or model-dependent (unknown magnetic field strength, small scale turbulence rapid dissipation, etc.). Clues are needed and while the usual chemical age modeling is not satisfying (problem of unknown initial conditions), we present here a simple constraint based on basic chemistry: the absence of DCO<sup>+</sup> in dark cloud envelopes can only be explained if the clouds are young enough and we propose to determine an upper limit for this age which is as much independent from the initial conditions as possible.

## 2. The abundance of CO and DCO<sup>+</sup>, and the deuterium chemistry

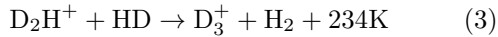
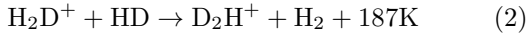
Dark clouds contain dust grains embedded in interstellar gas, itself mostly molecular as these clouds are self-shielded against our Galaxy's UV background. These dark clouds are cold (typically 10 K, with cores as low as 7 K, Pagani et al. 2003, 2005), and deep inside, where the density reaches a few  $10^4 \text{ cm}^{-3}$ , the heavy species freeze out onto grains to form ices. Both these ices and the gas are subject to a rich chemistry. Recently, strong deuteration (deuterium enhancement with respect to hydrogen carriers: DCO<sup>+</sup> versus HCO<sup>+</sup>, HDCO and D<sub>2</sub>CO versus H<sub>2</sub>CO, etc.) has been recognized as a useful tool to better understand both the chemistry itself and the star formation process (Bergin & Tafalla 2007; Ceccarelli et al. 2007).

H<sub>2</sub> is the main hydrogen reservoir in dark clouds, and similarly, HD is the main deuterium reservoir. Its relative abundance to H<sub>2</sub> is  $\sim 3 \times 10^{-5}$  (Hébrard 2006; Linsky et al. 2006). Watson (1976) was the first to invoke chemical deuterium enrichment via the important reaction



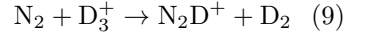
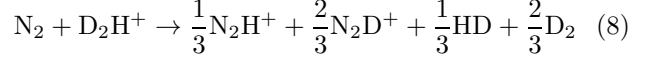
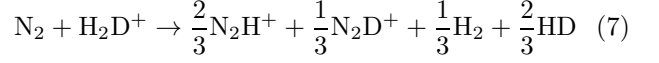
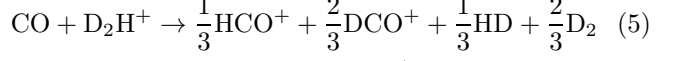
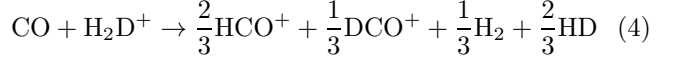
$\Delta E = 232 \text{ K}$  when all species (reactants and products) are in their ground state. In cold dark clouds, the forward reaction is strongly favorable, creating H<sub>2</sub>D<sup>+</sup>/H<sub>3</sub><sup>+</sup> ratios much larger than the original HD/H<sub>2</sub> ratio. If CO is abundant ( $X[\text{CO}] \approx 1.5 \times 10^{-4}$ , where  $X[\ ]$  denotes the relative abundance of a species with respect to H<sub>2</sub>), H<sub>3</sub><sup>+</sup> reacts 5 times more often with CO than with HD, and forms HCO<sup>+</sup>, strongly decreasing the abundance of H<sub>2</sub>D<sup>+</sup>.

Once H<sub>2</sub>D<sup>+</sup> is formed, it can be enriched in deuterium by reacting with HD again to form D<sub>2</sub>H<sup>+</sup> and D<sub>3</sub><sup>+</sup> as first recognized by Roberts et al. (2003):

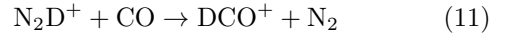
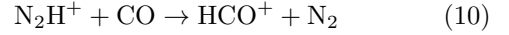


These two reactions are again favorable in the forward direction at low temperatures because of their exothermicity. Then, these H<sub>3</sub><sup>+</sup> isotopologues

can easily transfer their deuterons to other species:



When CO is abundant, H<sub>2</sub>D<sup>+</sup> is much less abundant as noted above and also reacts with CO preferentially, quenching all the other deuteration paths. CO also reacts with species like N<sub>2</sub>H<sup>+</sup> and N<sub>2</sub>D<sup>+</sup> to destroy them:



The strong correlation between CO freeze-out onto grains and deuteration (e.g. Crapsi et al. 2005) confirm the chemical models (e.g. Roberts et al. 2003) as sketched above and has led to the conclusion that CO freeze-out was necessary for strong deuteration to occur. There is however one exception to this statement: the deuteration of CO itself can form DCO<sup>+</sup>. In first approximation, if H<sub>3</sub><sup>+</sup> is mainly destroyed by CO,  $X[\text{H}_2\text{D}^+]$  varies like  $X[\text{CO}]^{-1}$ , whereas the production of DCO<sup>+</sup> is proportional to  $X[\text{CO}]$  and  $X[\text{H}_2\text{D}^+]$  (reaction 4). Thus the dependency upon  $X[\text{CO}]$  cancels out and  $X[\text{DCO}^+]$  should remain approximately constant. Figure 1 shows the abundance of  $X[\text{DCO}^+]$ ,  $X[\text{H}_3^+ \text{ isotopologues}]$  and  $X[\text{N}_2\text{D}^+]$  as a function of  $X[\text{CO}]$  in a steady-state chemical model. The  $X[\text{H}_3^+ \text{ isotopologues}]$  is the sum of the abundances of all 3 deuterated H<sub>3</sub><sup>+</sup> isotopologues, which represent altogether the main deuteration partners of species like CO and N<sub>2</sub>. The model is the same as in Pagani et al. (2009) but CO now runs from an undepleted relative abundance of  $1.5 \times 10^{-4}$  down to a depletion by a factor 300 ( $X[\text{CO}] = 5 \times 10^{-7}$ ), for a cloud density of  $10^4 \text{ cm}^{-3}$  at 10 K. When  $X[\text{CO}]$  starts to drop,  $X[\text{H}_3^+ \text{ isotopologues}]$  increases faster than proportional (indicated by the -1 slope) because the D<sub>2</sub>H<sup>+</sup> abundance depends both on the destruction of H<sub>3</sub><sup>+</sup> by CO and on the destruction of H<sub>2</sub>D<sup>+</sup> by CO, and

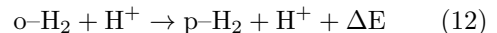
the  $D_3^+$  abundance depends also on the destruction of  $D_2H^+$  by CO. This explains that at the beginning,  $X[DCO^+]$  increases: the deuteration capabilities increase faster than  $X[CO]$  decreases. While  $X[CO]$  keeps decreasing, the deuteration capabilities reach saturation and  $X[DCO^+]$  becomes proportional to  $X[CO]$  (traced by the +1 slope).  $X[N_2D^+]$ , a representative gas-phase deuterated species, follows the deuteration capabilities of the cloud, as expected. It is clear that  $DCO^+$  has a behavior different from the other deuterated species, with an abundance varying only by 50% while the CO abundance drops by a factor of 30, and most importantly by *reaching its maximum abundance when CO is high* and deuteration capabilities are down. Therefore, one would expect  $DCO^+$  to be present everywhere in the cloud. It is not the case. Indeed,  $DCO^+$  is, as the other deuterated species, only detected in the depleted prestellar cores on extents similar to  $NH_3$  (Butner et al. 1995; Juvela et al. 2002) and nowhere else. This can only be explained if a high  $H_2$  OPR is present. Indeed the  $H_2$  OPR is an important controller of the cold cloud deuteration chemistry, as already discussed in Pineau des Forêts et al. (1991); Flower et al. (2006) and Pagani et al. (1992, 2009).

### 3. The role of ortho- $H_2$

$H_2$  has 2 different possible nuclear spin states due to the proton spin of  $\frac{1}{2}$ : parallel (ortho,  $I = 1$ , weight  $2I+1 = 3$ ) and anti-parallel (para,  $I = 0$ , weight = 1). The ortho state corresponds to the odd rotational levels ( $J = 1, 3, 5, \dots$ ), the para state to the even levels. The first ortho state ( $J = 1$ ) is 170 K above the ground ( $J = 0$ ) para state. The ortho-para exchange is possible neither via radiative processes, nor via inelastic collisions. It can occur in the gas phase and on the surface of dust grains (Le Bourlot 2000). The conversion rate on a solid surface is however highly uncertain (Watanabe et al. 2010; Chehrouri et al. 2011) and it is most probable that this is mainly realized by gas-phase chemical reactions with  $H^+$  or  $H_3^+$  ions (Dalgarno et al. 1973; Flower & Watt 1984; Le Bourlot 1991; Flower et al. 2006). The importance of ortho- $H_2$  in the deuteration process was first studied by Pineau des Forêts et al. (1991); Pagani et al. (1992), and later on, Flower et al. (2006) revealed its importance as a deuteration regulator. However, they considered the consequences

of the OPR evolution only for the prestellar core formation itself. In a study of L183 main prestellar core, Pagani et al. (2009) noted that the  $H_2$  OPR evolution timescale required by the observed  $N_2D^+/N_2H^+$  ratio was on the order of the free-fall time. They also noted that the OPR had to drop below 0.01 for  $N_2D^+$  to become detectable.

The  $H_2$  OPR value is not easily accessible.  $H_2$  does not emit in cold dark clouds and is seen only in shocked regions, especially protostar outflows, or in absorption in UV in low extinction regions. The energy release from the  $H_2$  formation reaction, assumed to be 1.5 eV in the equipartition hypothesis, is large enough to populate many levels of both ortho and para species: it is hence generally accepted, though not certain, that the OPR is 3:1 when  $H_2$  forms on grains. Once released in the gas phase,  $H_2$  tends to relax towards its thermal equilibrium state but never reaches it because at trace abundance levels, ortho- $H_2$  destruction is compensated by fresh  $H_2$  formed onto grains from residual H and from destruction of ions such as  $H_3^+$  and  $H_2D^+$  that can release an ortho- $H_2$  (Le Bourlot 1991; Flower et al. 2006). It is therefore necessary to model the chemical evolution of the  $H_2$  OPR to understand the evolution of dark clouds. Once  $H_2$  is formed, it can react with  $H^+$  and  $H_3^+$  to exchange states (Le Bourlot 1991; Flower et al. 2006). For example,



$\Delta E = 170$  K is the energy released as  $H_2$  goes from  $J=1$  to  $J=0$  levels. The reverse endothermic reaction is thus difficult to obtain in a cloud at 10 K and ortho- $H_2$  slowly decreases to low abundance levels ( $\approx 10^{-3} - 10^{-4}$ ). Similarly, in reaction 1, except for HD, all the species have ortho and para states and  $\Delta E$  therefore depends in fact on the considered initial and final states. If only para states are involved in the products,  $\Delta E$  is maximal ( $\Delta E = 232$  K with para- $H_3^+$  and 265 K with ortho- $H_3^+$ , HD being always in its ground state,  $J = 0$ ) but if both products are in their ortho ground state while the reactants are in their lowest state, para- $H_3^+$  ground state and HD ( $J = 0$ ),  $\Delta E$  becomes negative and the reaction is slightly endothermic ( $H_2D^+$  lowest ortho state is 87 K above the para ground state, and the total required energy is 25 K). Similarly, while the reverse reaction is impossible in a 10 K cloud with both para reactants,

it becomes rapid with ortho- $\text{H}_2\text{D}^+$  and ortho- $\text{H}_2$  even at 10K, as this channel is slightly exothermic ( $\Delta E = 25$  K) to produce para- $\text{H}_3^+$ . A few such channels are opened with ortho- $\text{H}_2$  allowing the efficient destruction of the  $\text{H}_3^+$  deuterated isotopologues. Ortho- $\text{H}_2$  is thus an important chemical poison to deuteration in dark clouds. Its abundance is therefore critical to control the deuteration enhancement (Flower et al. 2006; Pagani et al. 2009). Because  $\text{DCO}^+$  is not observed everywhere in the clouds outside the depleted cores where it is detected (Butner et al. 1995; Juvela et al. 2002) while its abundance should be maximal, this sets a minimum level for the abundance of ortho- $\text{H}_2$ . In turn, this minimum level gives rise to an upper limit to the age of the cloud, as ortho- $\text{H}_2$  abundance must eventually decrease to low levels as implied by reaction (12), and in order to explain the deuteration enhancements seen in the depleted cores, which, in some cold cores, can become huge (amplification up to  $10^{12}$ , Lis et al. 2002; van der Tak et al. 2002; Parise et al. 2004).

#### 4. The chemical model

To address these questions, we used the deuteration network from Roueff et al. (2005, 2007) in which we have included the ortho-para chemistry as described in Pagani et al. (2009), based itself on the work by Walmsley et al. (2004); Flower et al. (2006) and the new rate coefficients of Hugo et al. (2009). We have also included analytical approximations of the spin state-dependent dissociative recombination rates of  $\text{H}_3^+$  isotopologues from the tables in Pagani et al. (2009). The deuteration network includes all simple species (up to 6 atoms) based on C, N, O, and S with up to 5 deuterium substitutions ( $\text{CD}_5^+$ ). For those reactions with a small endothermicity ( $E/k_B < 600$  K), we have corrected the endothermicity when the reaction with ortho- $\text{H}_2$  was involved (e.g.,  $\text{CD} + \text{H}_2 \rightarrow \text{CH} + \text{HD}$  is endothermic with para- $\text{H}_2$  and exothermic with ortho- $\text{H}_2$ ). For all reactions with rare species producing  $\text{H}_2$  (e.g.,  $\text{HCN}^+ + \text{H} \rightarrow \text{CN}^+ + \text{H}_2$ ), we have always assumed that  $\text{H}_2$  is released in its para form, the most favorable energetically (similarly, only ortho- $\text{D}_2$  is considered in similar reactions with deuterated species). This does not noticeably accelerate the decay of ortho- $\text{H}_2$ . We checked that after, e.g.,  $10^5$  years, the para- $\text{H}_2$  production rate is 99.9% dominated

by reactions of ortho- $\text{H}_2$  with  $\text{H}_3^+$  and  $\text{H}^+$ . Our model is not aimed at reproducing accurately a given cloud but it allows to follow the evolution of the  $\text{H}_2$  OPR in a molecule rich gas. We have computed the chemical evolution of a cloud of constant density ( $n(\text{H}_2) = 10^4 \text{ cm}^{-3}$ ), constant temperature (10 K), average grain radius of  $0.1 \mu\text{m}$  and cosmic ionization rate of  $1 \times 10^{-17} \text{ s}^{-1}$ , which represent the usual conditions met in starless dark clouds. We have started with all species being atomic except H which is considered to be already entirely converted to  $\text{H}_2$  and D to HD and we have considered different OPR starting ratios from 3 down to  $3 \times 10^{-3}$  to account for the possibility of  $\text{H}_2$  production OPR below 3. Figure 2 shows the evolution of  $\text{DCO}^+$  and ortho- $\text{H}_2$  with time. We have traced the detectability limit of  $\text{DCO}^+$  for a cloud with a  $\text{H}_2$  column density of  $10^{22} \text{ cm}^{-2}$ , considering that a  $\text{DCO}^+$  J:1 $\rightarrow$ 0 line with a width of  $0.5 \text{ km s}^{-1}$  and an intensity of 0.1 K would be easily detectable with present day radiotelescopes. With the RADEX non-LTE radiative transfer model (van der Tak et al. 2007), we find that a  $\text{DCO}^+$  column density of  $\sim 2 \times 10^{11} \text{ cm}^{-2}$  is detectable, equivalent to a relative abundance to  $\text{H}_2$  of  $\sim 2 \times 10^{-11}$ . Figure 2 shows that for any initial  $\text{H}_2$  OPR below 0.1,  $\text{DCO}^+$  should be detected throughout the cloud in less than  $3 \times 10^5$  years. For an initial OPR = 0.1, the  $\text{DCO}^+$  becomes marginally detectable around  $\sim 5 \times 10^5$  years, disappears and finally becomes clearly detectable after 2 My. For OPR > 0.1, it takes 3 to 6 million years to become detectable, i.e. when the  $\text{H}_2$  OPR drops below  $\sim 0.03$ . Compared to the  $\text{H}_2$  OPR drop from 3 to  $\sim 0.01$  in depleted cores which takes less than  $2 \times 10^5$  years to happen (Pagani et al. 2009), the difference is twofold: as density increases during the prestellar core formation, 1) the chemistry accelerates, and 2) depletion sets in and  $\text{H}^+$  is no more destroyed by the other species which have now disappeared from the gas phase ( $\text{H}_3^+$  becomes also more abundant but to a lesser extent).  $\text{H}^+$  can even become the dominant ion. The higher abundance of  $\text{H}^+$  and  $\text{H}_3^+$  and the accelerated chemistry provoke the rapid decline of ortho- $\text{H}_2$ .

On the same figure, we also trace the abundance of the sum of the deuterated  $\text{H}_3^+$  isotopologues in the case  $\text{H}_2$  OPR = 3. It shows that under 1 My, deuteration is dominated by the carbon chemistry

( $\text{CH}_2\text{D}^+$ ,  $\text{C}_2\text{HD}^+$ , etc.) which is not dependent upon the ortho- $\text{H}_2$  abundance due to exothermicities close to 400 K. It is only beyond 1 My that the  $\text{H}_3^+$  deuteration network takes over when ortho- $\text{H}_2$  starts to be negligible. If ortho- $\text{H}_2$  is low since the beginning, then the  $\text{H}_3^+$  isotopologue contribution to the abundance of  $\text{DCO}^+$  is important from the start which explains the disappearance of the dip between 1 and  $\sim 3$  My.

The model is also sensitive to two other initial conditions: the abundance of metals and the cosmic ray ionization rate. Metals, especially alkali and alkaline earth metals like Ca, Na, K, and others like Fe, have a direct influence on the electronic equilibrium of the chemical model which in turn changes the dissociative recombination efficiency for  $\text{DCO}^+$  and therefore its abundance. For standard  $\zeta$  ( $1 \times 10^{-17} \text{ s}^{-1}$ ) and  $\text{H}_2$  OPR (3), we have varied their abundance from  $3.4 \times 10^{-8}$  to  $1.3 \times 10^{-7}$ . For the lowest abundance (50% of the default one),  $\text{DCO}^+$  becomes detectable much earlier ( $2 \times 10^5 \text{ y}$ ) than in the standard case, drops below the detectability limit after 1 My and is detectable again after 4 My. For the highest abundance (twice the default one),  $\text{DCO}^+$  is detectable after 7.5 My. The cosmic ray ionization rate (Fig. 3): if the rate increases, the production of  $\text{H}^+$  and  $\text{H}_3^+$  increases, therefore accelerating the decay of ortho- $\text{H}_2$  and increasing the abundance of  $\text{HCO}^+$  and  $\text{DCO}^+$ . For  $\zeta = 3 \times 10^{-17} \text{ s}^{-1}$ ,  $\text{DCO}^+$  becomes detectable in less than  $10^5$  years. Values of  $\zeta$  in between 1 and  $3 \times 10^{-17} \text{ s}^{-1}$  would bring our model in agreement with some recent estimates of cloud lifetime (Enoch et al. 2008; Hatchell & Fuller 2008). Conversely, for  $\zeta = 3 \times 10^{-18} \text{ s}^{-1}$ , the chemistry is considerably slowed down,  $\text{DCO}^+$  becomes detectable only after 28 My and steady-state is reached only after 47 My. It must be noted however that such a low ionization rate seems unlikely following Padovani et al. (2009).

## 5. Conclusions

Ortho- $\text{H}_2$  abundance is most probably the main limiting parameter for  $\text{DCO}^+$  production. The absence of  $\text{DCO}^+$  outside depleted cores, while its abundance is expected to be maximum for CO abundances close to  $10^{-4}$ , is due to a high ortho- $\text{H}_2$  abundance in dark clouds ( $\text{OPR} \geq 0.1$ ) maintained long enough. Such high abundance

can survive thanks to low  $\text{H}^+$  and  $\text{H}_3^+$  abundances, remaining low via charge or proton exchanges with many neutral species. However, ortho- $\text{H}_2$  eventually disappears. This sets an upper limit to the age of  $\text{DCO}^+$ -quiet dark clouds of 3–6 million years after  $\text{H}_2$  has formed for the most probable initial conditions. Higher cosmic ray ionization rates would increase the abundance of  $\text{H}^+$  and  $\text{H}_3^+$  and can thus only shorten the maximal possible age of the clouds to values which are too small while lower rates would tend to relax the age constraint but seem very unlikely. This result strengthens the results of Hartmann et al. (2001); Enoch et al. (2008); Hatchell & Fuller (2008) and is not compatible with those of Tassis & Mouschovias (2004) and Mouschovias et al. (2006). From the chemical point of view, cold dark clouds seem to be really short-lived.

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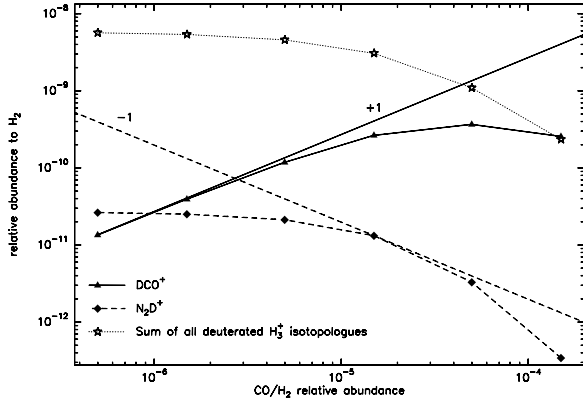


Fig. 1.—  $\text{DCO}^+$ ,  $\text{N}_2\text{D}^+$  and  $\text{H}_3^+$  isotopologues abundances as a function of CO abundance in a steady state model. Slopes of +1 and -1 are traced to better visualize the variation slope of the different ions.  $\text{DCO}^+$ , on the contrary to other deuterated species like  $\text{N}_2\text{D}^+$  reaches its maximum abundance for high CO abundances.

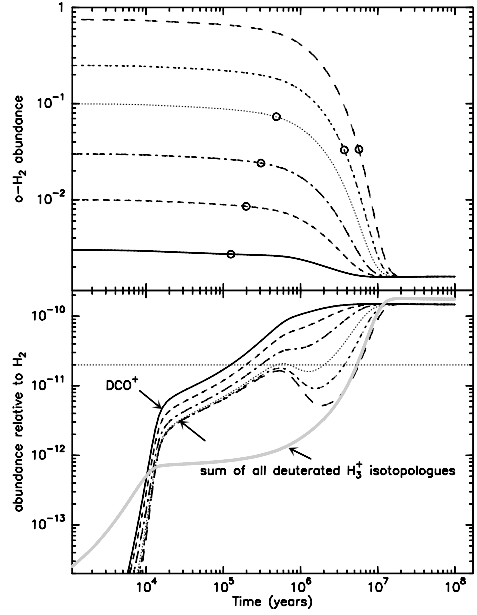


Fig. 2.— Variation of  $\text{DCO}^+$  and ortho- $\text{H}_2$  abundances in a pseudo time-dependent chemical model for different starting  $\text{H}_2$  OPRs from  $3 \times 10^{-3}$  up to 3. The abundance of the sum of the deuterated  $\text{H}_3^+$  isotopologues is also traced as a thick gray line (for the case  $\text{H}_2$  OPR = 3). The horizontal dotted line in the lower box indicates the limit of detection of  $\text{DCO}^+$  and the circles in the upper box mark the corresponding OPR values.

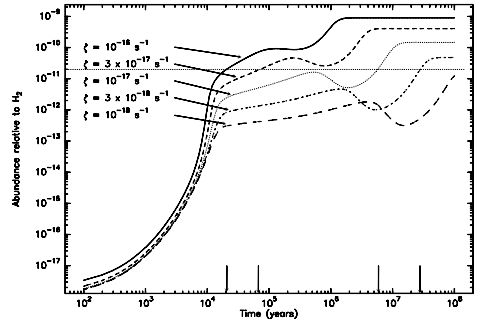


Fig. 3.— Variation of  $\text{DCO}^+$  and ortho- $\text{H}_2$  abundances in a pseudo time-dependent chemical model for different cosmic ray ionization rates from  $1 \times 10^{-18}$  up to  $1 \times 10^{-16}$ . The horizontal dotted line indicates the limit of detection of  $\text{DCO}^+$ , the arrows mark the time at which  $\text{DCO}^+$  abundance crosses the detection limit.